

## PATENT SPECIFICATION

NO DRAWINGS

991936



Date of Application and filing Complete Specification: July 10, 1961.

No. 24825/61.

Application made in United States of America (No. 41805) on July 11, 1960.

Application made in United States of America (No. 77027) on Dec. 20, 1960.

Complete Specification Published: May 12, 1965.

© Crown Copyright 1965.

Index at acceptance:—C3 P(4A, 4D1A, 4T2A, 4T2X); C2 C(1K2A3, 1K2C2, 3A16, 3C5A1, 3C5A2, 3C5C4, 3C5C5, 3C5E2, 3C6); C8 U5; D1 P(A1, A12, A17, B2B1, B4D, B5A, C2A10, C2A12A10, C2A12B2, C2C7, C2C9, C2C18)

Int. Cl.:—C 08 f // C 07 c, C 08 b, D 06 m

## COMPLETE SPECIFICATION

### Chemical Products, including Chemically Modified Polymeric Materials and processes for preparation thereof

- We, J. P. STEVENS & CO., INC., a corporation organised under the laws of the State of Delaware, United States of America, of 1460 Broadway, New York, New York, United States of America do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 5 The present invention relates to chemically modified polymeric materials and processes for the manufacture thereof.
- 10 More particularly, the present invention relates to processes of reacting soluble polymeric materials containing a plurality of free hydroxyl groups per polymeric molecule with polyfunctional compounds and products produced thereby.
- 15 The soluble polymeric materials employed in the present invention are those having free hydroxyl groups and include polyvinyl alcohol, starch and the like. The invention also contemplates the reaction of soluble polymers containing active hydrogen atoms (other than the hydrogens in the hydroxyl groups), including polyamines, polyamides, keratins, and the like with polyfunctional compounds.
- 20 As used in this specification the term 'active hydrogen atoms' means that the materials treated contain active hydrogen atoms as determined by the Zerewitinoff method.
- 25 Various embodiments of the invention are described hereinafter in connection with processes for reacting soluble polymers containing a plurality of hydroxyl groups per polymeric molecule, with polyfunctional sulfones to produce sulfone ethers having valuable and highly desirable properties which render them useful in the textile and other arts.
- 30 Applicant has made the unexpected discovery that it is possible to react substituted and unsubstituted beta oxyethyl sulfones such as polyhydroxyethyl or poly - alkoxyethyl sulfones with free hydroxyl containing soluble polymeric materials under mild reaction conditions and in the virtual absence of water. Short reaction times and moderate temperatures may be employed in the presence of mildly alkaline catalysts. When strong alkaline catalysts are used, the amount required is low so that damage to the polymer is avoided even in the presence of strong alkali. For example concentrations of alkali hydroxide ranging from about 0.5% to about 5%, based on the weight of the solution used are effective. Since the reaction between the beta - oxyethyl sulfones and the polymer takes place on heating after the water has been essentially removed from the system, the presence of a strong alkaline catalyst under these conditions does not dissolve or degrade the polymer. The necessity for employing expensive, toxic, or otherwise commercially objectionable reagents to effect crosslinking of polymeric materials is also avoided since the beta-oxyethyl sulfones and the alkaline catalysts are easily handled in commercial equipment without requiring special ventilation, corrosion-proof equipment or unusual safety precautions.
- 35 It is an object of the present invention to provide new and useful polymeric materials which are prepared by crosslinking soluble polymeric materials containing a plurality of free hydroxyl groups per polymeric molecule with polyfunctional sulfone compounds.
- 40 It is a further object of the present invention to provide a novel process for crosslinking soluble polymeric materials containing a plurality of free hydroxyl groups per polymeric molecule which will not require heating in the presence of an acidic catalyst, or treatment in the presence of high concentrations of strong aqueous alkali, thereby avoiding degradation of said materials.

It is a further object of this invention to provide a novel process for crosslinking the aforementioned polymeric materials by employing reactants which do not contain or liberate odoriferous, lachrymatory or vesicant components during the reaction.

According to the invention there is provided a process for the production of cross-linked polymeric materials which comprises treating in the presence of an alkaline compound a soluble polymeric material containing a plurality of free hydroxyl groups per polymeric molecule or active hydrogen atoms as herein defined (other than the hydrogens in hydroxyl groups) with polyfunctional sulfones having the following general formula,



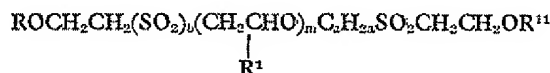
wherein M is  $\text{ROCH}_2\text{CH}_2\text{—}$  or  $(\text{ROCH}_2\text{CH}_2\text{SO})_{n-1}\text{Q—}$ ,

R being hydrogen or an alkyl group having from 1 to 5 carbon atoms. Q being an organic radical and n representing the valence of Q and having a value of 2 to 4. A particular group of sulfones suitable for use in the present invention are those having the formula



R, Q and n having the same meanings as in formula (I).

(IV)



in which a has a value from 0 to 5, b has a value from 0 to 1, m has a value from 0 to 5, but if m has a value of 1 to 5, then a has a value of 2 to 3 only, and b is 0 only if both a and m are 0, R and R<sup>11</sup> are hydrogen or an alkyl group having from 1 to 4 carbon atoms,

(V)



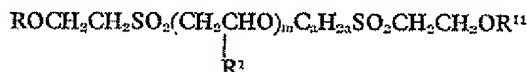
where n has a value from 2 to 12.

Included among the sulfones of formula (II) are sulfones which are expressed by the following formula:



where R is hydrogen or an alkyl group having from 1 to 4 carbon atoms, Q is an organic radical, and n represents the valence of Q and has a value of 3 to 4.

(VIII)



For purposes of this invention soluble polymeric materials containing a plurality of free hydroxyl groups are designated as  $\text{Pol—OH}$ , Pol representing the residue of a polymeric molecule minus the hydroxyl groups.

A preferred group of the aforementioned sulfones coming within the scope of formula I are the bis beta - hydroxyethyl and bis beta-alkoxyethyl sulfones of the formula:

(III)



where R is hydrogen or an alkyl group having from 1 to 4 carbon atoms, i.e.  $\text{CH}_3$  to  $\text{C}_4\text{H}_9$ , and where a has a value of 0 or 1, and Q is an organic radical such as an aliphatic, aromatic, or alkylaromatic residue.

While compounds coming within the scope of the formula I, II and (III) above can generally be used for the process of this invention, those which are soluble in water are particularly desirable, since the use of solvents other than water for commercial processing of polymeric materials is costly or hazardous, and often both. The water solubility of the compounds represented by the foregoing formulas is largely a function of the structure of the group Q, and we have found that compounds of the following formula have excellent water solubility, coupled with extraordinary effectiveness in the cross-linking reaction:

and R<sup>1</sup> is selected from the group consisting of hydrogen and methyl.

In addition a group of compounds related to Formula IV compounds have also proven effective in cross-linking polymeric materials and correspond to the formula



where R is hydrogen or an alkyl group having from 1 to 4 carbon atoms, n is the valence of Q and has a value of 2 to 4 and Q is an alkyl, aromatic, or alkylaromatic radical containing at least 3 carbon atoms. Additional sulfones contemplated by formulas (VI) and (VII) above include those expressed by the formula:

where R and R<sup>11</sup> are hydrogen or an alkyl group having from 1 to 4 carbon atoms, and in which a is an integer from 1 to 5, m has a value from 0 to 5, but if m has a value of 1 to 5, then a has a value of 2 to 3 only; and if m is 0, then a has a value of at least 3; the

(IX)



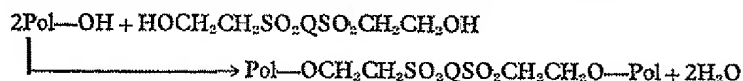
where R, and R<sup>11</sup> have the same meaning as in formula (VIII) above, a has a value from 1 to 5 and b has a value from 1 to 3.

The new reaction products or crosslinked polymeric ethers are obtained by reacting poly-

—C<sub>n</sub>H<sub>2a+1</sub>— moiety can be branched or straight chained; and R<sup>1</sup> is selected from the group consisting of hydrogen and methyl.

Still further sulfones contemplated by formulas (VI) and (VII) above include:

meric materials containing a plurality of free hydroxyl radicals per polymeric molecule, namely, Pol—OH, with the sulphones of formulae I to (IX) above. By way of example, this reaction is illustrated by:



where Q has the same meaning as in Formula I above.

The reaction between the sulfones disclosed herein and polymeric material can be carried out, for example, by contacting the polymer with a solution containing the sulfone and as a catalyst, an alkaline material such as an alkali salt of a weak acid (e.g. sodium acetate, potassium bicarbonate, alkali metal carbonate and the like) or an alkali hydroxide in low concentration or a non-volatile organic base, drying the polymer so treated, and heating the product thus treated for a brief period. Alternatively the polymer can be pretreated with the alkaline catalyst, then with the solution of the sulfone and thereafter dried and heated. On the other hand, the polymer can be pretreated with the sulfone solution, and the catalyst may be applied in a subsequent step. The choice of procedure depends in part on the solubility characteristics of the specific sulfone employed as a crosslinking agent. The concentration of the hydroxyethyl or alkoxyethyl sulfone employed will depend on the equivalent weight of the sulfone, on the extent of crosslinking which is desired, and on the range of properties which are sought for the material being treated.

Catalysts which are effective for the process of the invention are generally alkaline or potentially alkaline catalysts including non-volatile organic bases, alkali hydroxides and alkali salts of weak acids. The acetates and bicarbonates of an alkali metal are preferred since they are economical and do not cause discoloration when the polymer is heated in their presence. Alkali metal carbonates, hydroxides, phosphates, silicates and borates are also operative. Generally speaking, alkali salts of acids which have an ionization constant lower than 10<sup>-4</sup> may be used over a wide range of reaction conditions, while alkali hydroxides are effective only when the reaction conditions are carefully selected to minimize side reactions. Non-volatile organic bases may also be used.

Quaternary ammonium hydroxides are approximately equivalent in their effectiveness to alkali metal hydroxides. Non-volatile tertiary amines may also be used providing the pH of their aqueous solutions is about 10 or higher and providing also that their boiling point is sufficiently high to avoid evaporation of the catalyst during the drying step. For example, 1,1,3,3 - tetramethyl guanidine (b.p. 159—160°C) is moderately effective as a catalyst. Primary and secondary amines are not desirable catalysts since the hydrogen atoms linked to the amino groups react with the beta-oxysulfones, and the primary or secondary amine thus competes with the polymer for the available sulfone reagent.

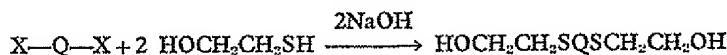
The concentration of catalyst required is a function of the amount of crosslinking agent employed, of the specific catalyst selected (equivalent weight and alkalinity), and of the time of heating. Concentrations ranging from about 5% to about 150% based on the weight of crosslinking agent are effective. When the alkaline catalyst employed is a strong base as for example in the case of alkali hydroxides and quaternary ammonium hydroxides, the amount used should be preferably between 5% and 50%, based on the weight of crosslinking agent employed, since larger amounts tend to cause discoloration and degradation of the polymer. When the alkaline catalyst is a weak base, as for example in the case of alkali acetates and bicarbonates, the amount used may be varied within wide limits and amounts varying from about 20% to about 150%, based on the weight of crosslinking agent employed may be used with excellent results. Larger amounts of catalyst generally tend to increase the reaction rate. When a tertiary amine is used as catalyst, the amount required depends on its ionization constant (as indicated by the pH of its aqueous solutions) and also on the amount which may be retained in the polymer in the course of drying and heating. This in turn depends on the vapor pressure of the amine compound, and

on the reaction conditions employed.

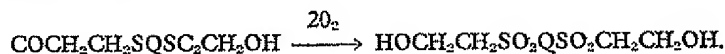
- 5 The time of heating which is required in order to bring the reaction to substantial completion ranges from about 10 seconds upward after removing the water present, and depends on the temperature of heating and the other reaction conditions selected. The preferred time range is about 30 seconds to five minutes. The temperature at which the reaction takes

place ranges from about 60°C. (140°F.) to about 200°C. (392°F.) with a preferred range being from about 100°C. to 180°C.

The sulfone compounds used in the present invention can be prepared, for example, by reacting a polyfunctional halide (X—Q—X) with 2-mercapto ethanol in the presence of an alkali hydroxide according to the following reaction:

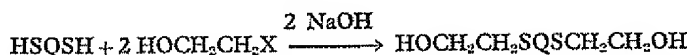


- 20 and oxidizing the thioether formed as follows:



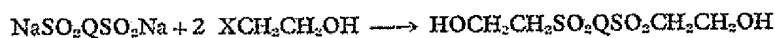
Alternatively, the compounds used in the present invention can be prepared by reacting a polymercaptan (HSQSH) with ethylene halo-

hydrin (HOCH<sub>2</sub>CH<sub>2</sub>X) in presence of alkali as follows:



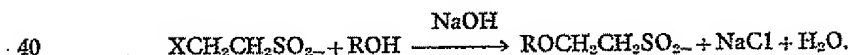
and oxidizing the thioether as shown above. They also can be prepared by reacting the alkali salt of a polyfunctional sulfinic acid

(NaSO<sub>2</sub>QSO<sub>2</sub>Na) with ethylene halohydrin (XCH<sub>2</sub>CH<sub>2</sub>OH) as follows:



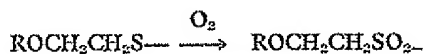
- 35 The ethers containing the grouping ROCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>— can be prepared by several methods. For example, it is known to prepare

the sulfone ethers from the corresponding sulfone halide and alcohol in presence of alkaline catalysts



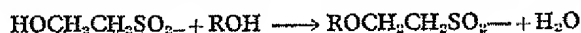
Alternatively, they can be prepared by oxidation of the corresponding alkoxyethyl sulfides:

alcohol in the presence of an alkaline catalyst:



- 45 In some instances they can also be prepared by addition of a vinyl sulfone compound to an

The ethers containing the grouping ROCH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>— can also be prepared from the corresponding hydroxyethyl sulfone compounds by direct reaction with an alcohol in presence of alkaline catalyst:



- 55 This reaction allowing the preparation of the ethers from two hydroxyl components takes place even in presence of a mild alkali such as the alkali carbonates and bicarbonates. The mechanism of the ether formation is related to that of the crosslinking reactions discussed on pages 10 and 11.

of water or from other beta alkoxyethyl sulfones by elimination of volatile alcohol in the presence of alkaline catalyst are greatly advantageous.

- 60 All these methods of preparation outlined above for the beta hydroxyethyl and beta alkoxyethyl sulfones give excellent yields of the desired compounds, and the choice of procedure can be based on the availability and cost of the raw materials involved. In the case of beta alkoxyethyl sulfones, the process in which the products are prepared directly from the beta hydroxyethyl sulfones by elimination

Of the Examples which follow, Examples I to XI describe methods of preparing various polyfunctional sulphones which Examples XII and XIII illustrate the process of the invention.

#### Preparation of the sulfones

##### EXAMPLE I

156 g (2 mol) of 2-mercaptoethanol are added with stirring to a solution of 80 g (2 mol) of sodium hydroxide in 80 g of water under a slow current of nitrogen. 143 g (1 mol) of 2,2' dichloroethyl ether are then added drop-

wise with vigorous stirring at 20°—30°C. The reaction mixture is then refluxed with stirring for about 4 hours, or until a titration for ionic chloride indicates that the reaction is substan-

tially complete. The mixture is then filtered to remove sodium chloride and concentrated under reduced pressure. The residue



10 is a viscous syrupy material, which crystallizes on standing, and can be converted to the corresponding bis-sulfone by oxidation, for example with hydrogen peroxide as follows:

15 Three grams of phosphoric acid are added, and 408 grams of 33% hydrogen peroxide are added dropwise with stirring and cooling at 30°—40° for the first half of the addition, then heating at the reflux temperature. The resulting

clear solution is refluxed for about 15 hours or until a potassium iodide test for hydrogen peroxide is negative.

After neutralizing the phosphoric acid catalyst, the mixture is subjected to vacuum distillation to remove the water. The residue is a viscous light yellow liquid which can be purified by solvent extraction and thereafter crystallized. It has the structure



#### EXAMPLE II

30 One hundred and fifty-six grams (2 mol) of 2 - mercaptoethanol are added with cooling and stirring to a solution of 80 grams (2 mol) of sodium hydroxide in 500 cc. of ethanol. A slow current of nitrogen is passed through the reaction mixture at all times in order to avoid oxidation of the mercaptan. 99 grams (1 mol —2 equivalents) of ethylene dichloride are then added with vigorous stirring and cooling. A precipitate of sodium chloride begins to form, and the reaction mixture is agitated at 40 70°—80°C (reflux) until an argentometric titration for ionic chloride indicates that the reaction is complete. This requires about 4 hours. The reaction mixture is filtered to remove precipitated sodium chloride, and concentrated under reduced pressure. The residue



% S calculated 26.0; found 25.95.

#### EXAMPLE III

When 1, 4 dichlorobutane is reacted with 2 - mercaptoethanol by the procedure described in Examples I and II, the bis-thioether obtained has the structure



This can be oxidized to the corresponding bis-sulfone, which is obtained as a water soluble crystalline power (m.p. 110°—115°C), after evaporating the water solution to dryness and washing the residue with acetone. % S calculated 23.4; found 24.0.

#### EXAMPLE IV

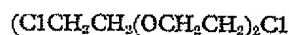
The reaction product of 2 - mercapto - ethanol with  $\zeta,\zeta^1$  - dichloroxylylene



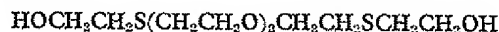
can be oxidized to the corresponding water insoluble bis - sulfone (m.p. 197—200°C), in accordance with Examples I and II above.

#### EXAMPLE V

From triethylene glycol dichloride:



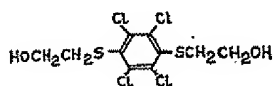
and 2 - mercaptoethanol there is obtained a bis-thioether



which on oxidation yields the corresponding syrupy liquid bis-sulfone which is completely soluble in water.

## EXAMPLE VI

From hexachlorobenzene, a bis thioether



- 5 (m.p. 148°—149°C) is obtained by the procedure described in J. Org. Chem. 24, 235 (1959). Oxidation with hydrogen peroxide yields the corresponding bis sulfone which is a water insoluble white crystalline solid (m.p. 200°—203°C.).

## EXAMPLE VII

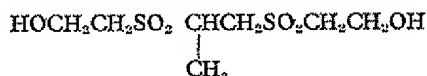
- 10 Bis  $\beta$  hydroxyethyl sulfide is converted to the corresponding sulfone



- 15 for example, by the procedure described in J. Org. Chem. 19, 1486 (1954). The product may be isolated in crystalline form (m.p. 52°—54°C.) or the crude aqueous solution may be employed without further purification.

## EXAMPLE VIII

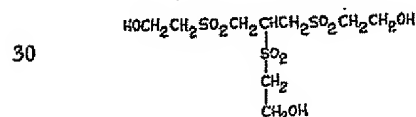
- 20 The bis hydroxyethyl sulfone



- 25 is prepared by reacting one mol of propylene dichloride (dichloropropane 1.2) with two mols of 2 - mercaptoethanol, and oxidizing the resulting bis - hydroxyethyl sulfide. The product is a water soluble crystalline solid, m.p. 125°—128°C.

## EXAMPLE IX

The tris-hydroxyethyl sulfone

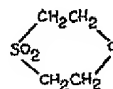


- 35 is prepared by reacting one mol of trichloropropane 1, 2, 3 with three mols of 2 - mercaptoethanol, and oxidizing the resulting tris - hydroxyethyl sulfide. The product is a water soluble crystalline solid, m.p. 147°—158°C.

## EXAMPLE X

- 40 A mixture of 154 grams (1 mol) of anhydrous bis beta hydroxyethyl sulfone (product of Example VII), 741 grams (10 mol) of n-butanol, 200 grams of xylol and 100 grams of anhydrous potassium bicarbonate are refluxed with vigorous mechanical stirring while the

water formed in the reaction is removed through a Dean-Stark moisture trap. The temperature of the reaction mixture when refluxing begins is about 112°C, and the temperature rises slowly to about 118° in the course of reaction. Refluxing is continued until the liberation of water is complete. This requires about 4—5 hours, and 33 grams (1.8 mols) of water are obtained. The reaction mixture is cooled to room temperature and filtered to remove the potassium bicarbonate catalyst which is recovered quantitatively. The filtrate is then stripped under reduced pressure, heating to about 120°—130°C at 25 mm. to remove xylol and unreacted butanol. Some crystalline material forms in the residue on cooling. This is filtered off, and identified as p - oxathiane 4-4, dioxide:



(m.p. 129°C). The amount of this by-product is 34 grams, corresponding to about 25% of the bis-beta hydroxyethyl sulfone employed for the reaction. The filtrate obtained after removal of the cyclic compound consists mainly of the desired product, namely the dibutyl ether



This may be purified by vacuum distillation to give a clear colorless liquid boiling at 184°—189°C/9 mm.

## EXAMPLE XI

354 grams of divinyl sulfone (3 mols) are added with stirring and cooling to a solution of 7.5 grams of sodium methylate in 240 grams (7.5 mols) of anhydrous methanol. The reaction is exothermic, and the temperature is controlled by regulating the rate of addition and by the use of an ice-water bath. The addition of the divinyl sulfone is carried out at 25 to 35°C and requires 3 hours. The reaction mixture is then heated to 60°, and kept at 60° for about 1 hour. The sodium methylate catalyst is then neutralized with 18 grams of acetic acid, the mixture is filtered to remove salts and the filtrate is distilled under reduced pressure. The product



is a water white liquid, boiling at 138—140°C at 6 mm. It is completely soluble in water and stable in aqueous solutions. The yield obtained in this manner is 450 grams or 83% of the theoretical.

*Reaction of the sulfones with soluble polymeric materials*

EXAMPLE XII

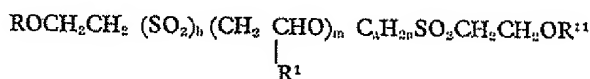
- 5 A cotton twill fabric is impregnated on a laboratory padder with a solution containing 30 grams per liter of polyvinyl alcohol resin (for example the product marketed under the trade name of Gelvatol 1—90 by the Shawinigan Resin Corporation), 30 grams per liter of the product of Example VII and 20 grams per liter of potassium bicarbonate. The pressure of the pad rolls is adjusted so that the fabric retains a weight of solution equal to its weight (100% wet pickup). The fabric so treated is dried at 200°F., cured 5 minutes at 300°F., and washed to remove soluble materials. In the course of this process the polyvinyl alcohol resin has been insolubilized, and the finish deposited on the fabric is not removed in laundering. If for example the stiffness of the treated cloth is measured by known methods, and compared with the stiffness of untreated cloth, and cloth treated with polyvinyl alcohol only, the following values are obtained.

	Stiffness value*	
	Initial	After 5 launderings
Fabric treated according to Example XII	20	35
Fabric treated with polyvinyl alcohol only	35	95
Untreated fabric	125	130

- 35 \*Expressed as the sum of the angles of deflection obtained in the warp and filling direction on a Monsanto crease recovery tester—Maximum stiffness = 0°; Minimum stiffness = 180°.
- 40 It is apparent that the stiffness of the fabric treated with polyvinyl alcohol only is lost in the course of laundering, and that the effect of the polyvinyl alcohol is retained through laundering by insolubilizing the resin size
- 45 according to our process.

EXAMPLE XIII

- 50 When the procedure of Example XII is repeated, using starch (for example, the product known as Kosol and manufactured by the National Starch and Chemical Co.) in place of polyvinyl alcohol, the following results are obtained:



- 105 wherein "a" has a value from 0 to 5, "b" has a value from 0 to 1, "m" has a value from 0 to 5 (but if "m" has a value of 1 to 5 then "a" is 2 or 3 and "b" is 0 only if "a" and "m" are

Fabric treated	Stiffness value		
	Initial	After 5 launderings	
according to Example XIII	30	45	55
Fabric treated with starch only	80	120	60
Untreated fabric	125	130	

Whenever desired, other finishing agents may be combined with the crosslinking agents of our invention in order to achieve other specific properties. For example, softeners, bacteriostatic agents, water repellents, stiffeners and the like may be included in the treating solutions if desired, without impairing the efficiency of the process. The choice of specific finishing agents is limited only by their chemical compatibility in the system, and within this framework of chemical stability, any mixture or combination of reactants may be used.

Sizing materials such as starch and polyvinyl alcohol resin may be insolubilized *in situ* (on the fibre, yarn or fabric) and thus rendered resistant to washing, as illustrated by Examples XII and XIII. Fibres manufactured from polyvinyl alcohol may also be improved by the cross linking treatments, since they are rendered resistant to water. Many others useful applications of the new processes are possible.

WHAT WE CLAIM IS:—

1. A process which comprises treating in the presence of an alkaline compound a soluble polymeric material containing a plurality of free hydroxyl groups per polymeric molecule or active hydrogen atoms as herein defined (other than the hydrogens in hydroxyl groups) with polyfunctional sulfones having one of the following general formulae



wherein M is  $\text{ROCH}_2\text{CH}_2$ — or  $(\text{ROCH}_2\text{CH}_2\text{SO}_2)_{n-1}\text{Q}$ —,

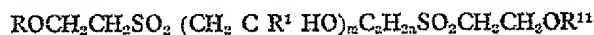
R being hydrogen or an alkyl group, having from 1 to 4 carbon atoms, Q being an organic radical and "n" representing the valence of Q and having a value of 2 to 4.

2. A process in accordance with claim 1 wherein the polymeric material is treated with a water-soluble beta oxyethyl sulfone of the following formula

0), R and R<sup>11</sup> are hydrogen or an alkyl group having from 1 to 4 carbon atoms and R<sup>1</sup> is hydrogen or methyl.

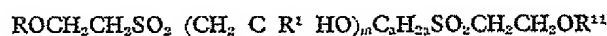
3. A process in accordance with claim 1

wherein the polymeric material is treated with a beta oxyethyl sulfone having the following general structure:—



- 5 wherein R and R<sup>11</sup> are hydrogen or an alkyl group having from 1 to 4 carbon atoms "a" is an integer from 1 to 5, "m" has a value of 0 to 5, "a" having value only of 2 or 3 when "m" has a value 1 to 5 and R<sup>1</sup> is hydrogen or methyl.

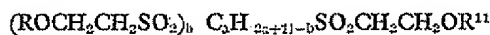
4. A process in accordance with claim 1 10 wherein the polymeric material is treated with a beta oxyethyl sulfone of the following formula:—



- 15 wherein "a" has a value of from 1 to 5, "m" has a value from 0 to 5 (but if "m" has a value of from 1 to 5 then "a" is 2 or 3 and if "m" is 0 then "a" at least 3, the "C<sub>2</sub>H<sub>5</sub>" portion being branched or straight-chained, R 20 and R<sup>11</sup> are hydrogen or an alkyl group having

from 1 to 4 carbon atoms and R is hydrogen or methyl.

5. A process in accordance with claim 1 25 wherein the polymeric material is treated with a poly beta hydroxy ethyl or alkoxyethyl sulfone having the formula:—



- 30 wherein R and R<sup>11</sup> are hydrogen or an alkyl group having from 1 to 4 carbon atoms, "a" has a value from 1 to 5 and "b" has a value from 1 to 3.

8. A process in accordance with any of the preceding claims wherein the alkaline compound is an alkaline salt of an acid having a ionization constant less than 10<sup>-4</sup>, e.g. an alkali metal carbonate or bicarbonate.

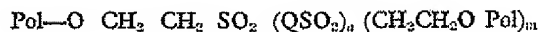
6. A process in accordance with any of claims 1—5 wherein the polymer is first contacted by the sulfone and thereafter by the alkaline 35 compound.

9. A process in accordance with any of the preceding claims wherein the reaction takes place at temperature of 100°C to 180°C.

7. A process in accordance with any of claims 1—5 wherein the polymer is first contacted by the alkaline compound and thereafter with the sulfone.

10. A process for the treatment of a soluble polymeric material substantially as described.

11. Cross linked polymers having the formula 50



- 55 wherein Pol represents a molecule of a soluble polymeric material having a plurality of hydroxyl groups but minus the hydroxyl groups, "Q" is an organic radical, "n" has a value of 0 to 3, "m" has a value of 1 to 3, and "m" is equal to "n" except where n=0 when m will be equal to 1.

12. Cross linked polymers from soluble 60 polymeric material substantially as described.

E. R. ROYSTON & CO.,  
Agents for the Applicants,  
Chartered Patent Agents,  
Tower Building, Water Street,  
Liverpool, 3.



991,936



## PATENT SPECIFICATION

NO DRAWINGS

991,936

Date of Application and filing Complete Specification: July 10, 1961.  
No. 24825/61.

Application made in United States of America (No. 41805) on July 11, 1960.

Application made in United States of America (No. 77027) on Dec. 20, 1960.

Complete Specification Published: May 12, 1965.

© Crown Copyright 1965.

Index at acceptance:—C3 P(4A, 4D1A, 4T2A, 4T2X); C2 C(1K2A3, 1K2C2, 3A16, 3C5A, 3C5A2, 3C5C4, 3C5C5, 3C5E2, 3C6); C3 U5; D1 P(A1, A12, A1 B2B1, B4D, B5A, C2A10, C2A12A10, C2A12B2, C2C7, C2C9, C2C1)

Int. Cl.:—C 08 f // C 07 c, C 08 b, D 06 m

## COMPLETE SPECIFICATION

**Chemical Products, including Chemically Modified Polymeric Materials and processes for preparation thereof**

We, J. P. STEVENS & CO., INC., a corporation organised under the laws of the State of Delaware, United States of America, of 1460

as polyhydroxyethyl or poly - alkoxyethyl sulfones with free hydroxyl containing soluble polymeric materials under mild reaction conditions

Bro:  
5 Stat  
tion  
grar  
to t  
in a  
10 T  
mod  
the  
A  
relai  
mer.  
15 hydroxy.  
polyfunctional  
duced thereby.

The soluble po.  
20 in the present inve  
hydroxyl groups an  
starch and the like. The invention also con-  
templated the reaction of soluble polymers  
containing active hydrogen atoms (other than  
25 the hydrogens in the hydroxyl groups), includ-  
ing polyamines, polyamides, keratins, and the  
like with polyfunctional compounds.

As used in this specification the term 'active  
hydrogen atoms' means that the materials  
30 treated contain active hydrogen atoms as  
determined by the Zerewitinoff method.

Various embodiments of the invention are  
described hereinafter in connection with pro-  
cesses for reacting soluble polymers containing  
35 a plurality of hydroxyl groups per polymeric  
molecule, with polyfunctional sulfones to pro-  
duce sulfone ethers having valuable and highly  
desirable properties which render them useful  
in the textile and other arts.

40 Applicant has made the unexpected dis-  
covery that it is possible to react substituted  
and unsubstituted beta oxyethyl sulfones such

as polyhydroxyethyl or poly - alkoxyethyl sul-  
fones with free hydroxyl containing soluble  
polymeric materials under mild reaction condi- 45

## ERRATA

SPECIFICATION No. 991,936  
Amendment No. 1

Page 4, line 21,  
for " $\text{COCH}_2\text{CH}_2\text{SQSC}_2\text{CH}_2\text{OH}$ "  
read " $\text{HOCH}_2\text{CH}_2\text{SQSCH}_2\text{CH}_2\text{OH}$ "

Page 4, line 70, for "alkoxyethyl" read  
"alkoxyethyl"

THE PATENT OFFICE  
25th October 1965

polymeric materials is also avoided since the  
beta-oxyethyl sulfones and the alkaline cata- 65  
lysts are easily handled in commercial equip-  
ment without requiring special ventila-  
tion, corrosion-proof equipment or unusual  
safety precautions.

It is an object of the present invention to  
provide new and useful polymeric materials  
which are prepared by crosslinking soluble  
polymeric materials containing a plurality of  
free hydroxyl groups per polymeric molecule  
with polyfunctional sulfone compounds. 75

It is a further object of the present invention  
to provide a novel process for crosslinking  
soluble polymeric materials containing a  
plurality of free hydroxyl groups per poly-  
meric molecule which will not require heating 80  
in the presence of an acidic catalyst, or treat-  
ment in the presence of high concentrations  
of strong aqueous alkali, thereby avoiding de-  
gradation of said materials.